

(19) 世界知的所有権機関  
国際事務局(43) 国際公開日  
2002 年 3 月 21 日 (21.03.2002)

PCT

(10) 国際公開番号  
WO 02/21938 A1(51) 国際特許分類<sup>7</sup>: A23L 1/22, 1/226, C07D 277/06

(21) 国際出願番号: PCT/JP01/07769

(22) 国際出願日: 2001 年 9 月 7 日 (07.09.2001)

(25) 国際出願の言語: 日本語

(26) 国際公開の言語: 日本語

(30) 優先権データ:  
特願2000-280451 2000 年 9 月 14 日 (14.09.2000) JP  
特願2000-280611 2000 年 9 月 14 日 (14.09.2000) JP  
特願2001-116509 2001 年 4 月 16 日 (16.04.2001) JP  
特願2001-116510 2001 年 4 月 16 日 (16.04.2001) JP

(71) 出願人 (米国を除く全ての指定国について): 味の素株式会社 (AJINOMOTO CO., INC.) [JP/JP]; 〒104-8315 東京都中央区京橋一丁目15-1 Tokyo (JP).

Mika) [JP/JP]. 西村康史 (NISHIMURA, Yasushi) [JP/JP]. 上田要一 (UEDA, Yoichi) [JP/JP]; 〒210-8681 神奈川県川崎市川崎区鈴木町1-1 味の素株式会社 調味料研究開発部内 Kanagawa (JP). 若林秀彦 (WAKABAYASHI, Hidehiko) [JP/JP]; 〒210-8681 神奈川県川崎市川崎区鈴木町1-1 味の素株式会社 食品研究所内 Kanagawa (JP). 香村正徳 (KOHMURA, Masanori) [JP/JP]; 〒210-8681 神奈川県川崎市川崎区鈴木町1-1 味の素株式会社 中央研究所内 Kanagawa (JP).

(74) 代理人: 霜越正夫, 外 (SHIMOKOSHI, Masao et al.); 〒103-0027 東京都中央区日本橋三丁目15-2 高愛ビル 9階 Tokyo (JP).

(81) 指定国 (国内): BR, CA, CN, ID, IN, JP, KR, MX, PH, SG, US.

(84) 指定国 (広域): ヨーロッパ特許 (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(72) 発明者; および

(75) 発明者/出願人 (米国についてのみ): 川口宏和 (KAWAGUCHI, Hirokazu) [JP/JP]. 宇田美佳 (UDA,

添付公開書類:  
— 国際調査報告書

[続葉有]

(54) Title: COMPOSITIONS FOR ENHANCING OR IMPROVING THE FLAVOR OF FOODS OR DRINKS AND METHOD OF ENHANCING OR IMPROVING THE FLAVOR OF FOODS OR DRINKS BY USING THE SAME

(54) 発明の名称: 飲食品の風味増強または改善組成物およびこれを使用する飲食品の風味増強または改善方法

(57) Abstract: A method of enhancing or improving the flavor of usual foods or drinks by using a non-volatile thiazolidine compound optionally together with a non-volatile flavor compound and/or a reaction flavor; a convenient and effective method for preventing deterioration in flavor in the step of pasteurizing a retort food and regulating its offensive smell at intake to thereby improve the flavor; and a convenient and effective method for regulating the greenish offensive smell characteristic to processed soybean product to thereby improve the flavor.

(57) 要約:

本願明細書には、不揮発性のチアゾリジン化合物を単独で使用し、またはこれに加えて不揮発性フレーバー化合物および/またはリアクションフレーバーを併用して、飲食物一般の風味を増強または改善する方法、ならびにレトルト食品の加熱殺菌時における風味劣化を抑制し、喫食時の不快臭を抑制してその風味を改善するための、簡便でかつ効果的な方法、および大豆利用食品における大豆特有の青臭い不快臭を抑制してその風味を改善するための、簡便でかつ効果的な方法が開示されている。

WO 02/21938 A1

**WO 02/21938**

Patent applicant: Ajinomoto Co., Inc.

Compositions for enhancing or improving the flavor of foods or drinks and method of enhancing or improving the flavor of foods or drinks by using the same

**Abstract:** A method of enhancing or improving the flavor of usual foods or drinks by using a non-volatile thiazolidine compound, or by using a non-volatile thiazolidine together with a non-volatile flavor compound and/or a reaction flavor; a convenient and effective method for preventing deterioration in flavor during the pasteurization of retort foods and regulating its offensive smell at intake, also a convenient and effective method of regulating the greenish offensive smell characteristic of processed soybean products, thereby improving the flavor.

**The patent claims**

1. Compositions for enhancing or improving the flavor of foods or drinks, characterized by having a non-volatile thiazolidine compound as the active component.
2. Compositions for enhancing or improving the flavor of foods or drinks described in claim 1, characterized by containing a non-volatile flavor compound in which a volatile flavor compound is stabilized by forming a disulfide bond with a non-volatile compound, and/or a reaction flavor, or using it together with a non-volatile thiazolidine compound.
3. Compositions for enhancing or improving the flavor of foods or drinks described in claims 1 or 2, characterized by being 1 or a mixture of compounds selected from thiazolidine compounds, with a structure in which polyhydroxyalkyl group derivatives with 3 to 11 carbon atoms are combined with a second carbon atom of thiazolidine -4- carboxylic acid.
4. Compositions for enhancing or improving the flavor of foods or drinks described in claim 3, characterized by being 1 or a mixture of compounds selected from the following non-volatile thiazolidine compounds: 2- (1,2,3- trihydroxy propyl) thiazolidine -4- carboxylic acid, 2- (1,2,3,4- tetrahydroxybutyl ) thiazolidine -4- carboxylic acid, 2- (1,2,3,4,5- pentahydroxy pentyl) thiazolidine -4- carboxylic acid, 2- Hydroxymethyl -2- (1,2,3,4- tetrahydroxybutyl ) thiazolidine -4- carboxylic acid, 2- (1,2,4,5- tetrahydroxy -3- glucopyranosyloxy pentyl) thiazolidine -4- carboxylic acid, 2- (1,2,3,4- tetrahydroxybutyl) thiazolidine -4- carbonyl -N- glycine, and 2- (1,2,3,4,5- pentahydroxy pentyl) thiazolidine -4- carbonyl -N- glycine.
5. Compositions for enhancing or improving the flavor of foods or drinks described in one of the claims 1 to 4, characterized by the content of a non-volatile thiazolidine compound being more than 1 ppm per dry matter of the composition.
6. Compositions for enhancing or improving the flavor of foods or drinks described in one of the claims 2 to 5, characterized by containing 1 – 1,000 ppm of a non-volatile thiazolidine compound and 1 – 1,000 ppm of a non-volatile flavor compound and/or a reaction flavor at the concentration of intake.
7. Manufacturing methods of foods or drinks characterized by using compositions for enhancing or improving the flavor of foods or drinks described in one of the claims 1 to 6.

8. Foods or drinks characterized by utilizing the manufacturing methods using compositions for enhancing or improving the flavor of foods or drinks described in claim 7.
9. New thiazolidine compounds and their salts described in the equation (2), characterized by R having the same structure as the residue of aldose or aldose type oligosaccharide, which is produced from the aldehyde group by removing an oxygen atom, or having the same structure as the residue of ketose or ketose type oligosaccharide, which is produced from carbonyl group by removing an oxygen atom.
10. Flavor improving methods for retort foods characterized by adding non-volatile thiazolidine compounds to retort foods to prevent deterioration in flavor.
11. Flavor improving methods for retort foods described in claim 10, characterized by using 1 or a mixture of compounds selected from thiazolidine compounds with the structure in which polyhydroxyalkyl group derivatives having 3 to 11 carbon atoms are combined with the second carbon atom of thiazolidine -4- carboxylic acid, as a non-volatile thiazolidine compound.
12. Flavor improving methods for retort foods described in claim 11, characterized by using 1 or a mixture of compounds selected from the following non-volatile thiazolidine compounds: 2- (1,2,3- trihydroxy propyl) thiazolidine -4- carboxylic acid, 2- (1,2,3,4- tetrahydroxybutyl ) thiazolidine -4- carboxylic acid, 2- (1,2,3,4,5- pentahydroxy pentyl) thiazolidine -4- carboxylic acid, 2- Hydroxymethyl -2- (1,2,3,4- tetrahydroxybutyl ) thiazolidine -4- carboxylic acid, 2- (1,2,4,5- tetrahydroxy -3- glucopyranosyloxy pentyl) thiazolidine -4- carboxylic acid, 2- (1,2,3,4- tetrahydroxybutyl) thiazolidine -4- carbonyl -N- glycine, and 2- (1,2,3,4,5- pentahydroxy pentyl) thiazolidine -4- carbonyl -N- glycine.
13. Flavor improving methods for retort foods described in one of the claims 10 to 12, characterized by adding a non-volatile thiazolidine compound before heat pasteurization in the retort food manufacturing process.
14. Flavor improving methods for retort foods described in one of the claims 10 to 13, characterized by the dosage of a non-volatile thiazolidine compound being 10 – 1,000 ppm for the food ingredients or weight of the retort food.
15. Flavor improving methods for retort foods described in one of the claims 10 to 14, characterized by using a non-volatile flavor compound and/or a reaction flavor, or using it together with a non-volatile thiazolidine compound.
16. Flavor improving methods for retort foods described in claim 15, characterized by adding 10 – 1,000 ppm of a non-volatile thiazolidine compound and 10 – 1,000 ppm of a non-volatile flavor compound and/or reaction flavor at the concentration of intake.
17. Retort foods characterized by being processed using a method described in one of the claims 10 to 16.
18. Flavor improving methods for soybean products, characterized by adding a non-volatile thiazolidine compound to soybean products to regulate the offensive greenish smell.
19. Flavor improving methods for soybean products described in claim 18, characterized by selecting 1 or more compounds from thiazolidine compounds with the structure in which polyhydroxyalkyl group derivatives having 3 to 11 carbon atoms are combined with the second carbon atom of thiazolidine -4- carboxylic acid, as a non-volatile thiazolidine compound.
20. Flavor improving methods for soybean products described in claim 19, characterized by using 1 or a mixture of compounds selected from the following

non-volatile thiazolidine compounds: 2- (1,2,3- trihydroxy propyl) thiazolidine -4- carboxylic acid, 2- (1,2,3,4- tetrahydroxybutyl ) thiazolidine -4- carboxylic acid, 2- (1,2,3,4,5- pentahydroxy pentyl) thiazolidine -4- carboxylic acid, 2-Hydroxymethyl -2- (1,2,3,4- tetrahydroxybutyl ) thiazolidine -4- carboxylic acid, 2- (1,2,4,5- tetrahydroxy -3- glucopyranosyloxy pentyl) thiazolidine -4- carboxylic acid, 2- (1,2,3,4- tetrahydroxybutyl) thiazolidine -4- carbonyl -N- glycine, and 2- (1,2,3,4,5- pentahydroxy pentyl) thiazolidine -4- carbonyl -N- glycine.

21. Flavor improving methods for soybean products described in one of the claims 18 to 20, characterized by adding a non-volatile thiazolidine compound to the soybean products before processing, during processing, or at the table just before eating.
22. Flavor improving methods for soybean products described in one of the claims 18 to 21, characterized by the dosage of a non-volatile thiazolidine compound being 10 – 1,000 ppm for the food ingredients or weight of the soybean product.
23. Flavor improving methods for soybean products described in one of the claims 18 to 22 characterized by using a non-volatile flavor compound and/or a reaction flavor, optionally, or using it together with a non-volatile thiazolidine compound.
24. Flavor improving methods for soybean products described in claim 23, characterized by adding 10 – 1,000 ppm of a non-volatile thiazolidine compound and 10 – 1,000 ppm of a non-volatile flavor compound and/or a reaction flavor at the concentration of intake.
25. Soybean products characterized by being processed utilizing methods described in one of the claims 18 to 24.

**Practical example 1:** synthesis of 2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carboxylic acid

17.56 g of cysteine hydrochloride (100 mmol) and 15.01 g of xylose (100 mmol) were dissolved in 35 ml of purified water. Then, 8.36 ml (100 mmol) of pyridine was added to the solution and agitated for 72 hrs at room temperature. 300 ml of ethanol was added and stored in a refrigerator to generate precipitation. The generated precipitation looked like a paste, and was dissolved into water, after the removal of the solvent by decantation. After Insoluble matters were removed by filtration, the solution was concentrated to make ca. 30 ml of concentrate. Ethanol was added to the concentrate, with an amount just a little short in producing precipitation. It was stored in a refrigerator for 12 hrs. The precipitation was collected by filtration and dried under reduced pressure. The same procedure was repeated two more times. Finally, 10.8 g of white powder was obtained. The molar yield versus cysteine was 42.7 %. Since the ion mass number of the obtained powder measured by an Electron Spray Ionization-Mass Spectrometry was equal to the molecular weight (molecular weight including hydrogen; 254) of the objective compound, the obtained powder was identified as the objective compound.

**Practical example 2:** synthesis of 2-(1,2,3,4,5-pentahydroxypentyl)thiazolidine-4-carboxylic acid  
(Omission)

**Practical example 3:** synthesis of 2-(1,2,4,5-tetrahydroxy3-glucopyranosyloxypentyl)thiazolidine-4-carboxylic acid

(Omission)

**Practical example 4:** The stability comparison of glutathione and cysteine.

2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carboxylic acid (TCA), one of non-volatile thiazolidine compound described in this patent, glutathione (GSH), and cysteine (Cys) were dissolved into a phosphoric acid potassium solution (50 mM of concentration), respectively, to make 5 mM of each solution. Each solution was adjusted to pH 7.0 using 1N sodium hydroxide solution, and stored at room temperature. The change of survival rate of each component in the proceeds of time was measured by a high-performance liquid chromatography. From the results obtained, TCA was better in stability compared with GSH and Cys.

**Practical example 5:** A sensory evaluation on bouillon soup.

A non-volatile thiazolidine compound, prepared by the method described in practical example 1, was added to a chicken bouillon (a commercial product) to make a 0.07 % solution (0.07 % is the concentration at eating). A sensory evaluation was conducted by 6 specialized panels. Chicken bouillon with non-volatile thiazolidine compound was stronger in flavor and more preferable compared with plain chicken bouillon.

**Practical example 6:** A sensory evaluation on egg soup.

(Omission)

**Practical example 7:** A sensory evaluation on corn soup.

(Omission)

**Practical example 8:** synthesis of a new compound, 2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carbonyl-N-glycine

(Omission)

**Practical example 9:** synthesis of a new compound, 2-(1,2,3,4,5-pentahydroxypentyl)thiazolidine-4-thiazolidine-4-carbonyl-N-glycine

(Omission)

**Practical example 10:** A sensory evaluation on beef bouillon soup.

(Omission)

**Practical example 11:** A sensory evaluation on instant coffee.

A thiazolidine compound, prepared by the method described in the practical example 8, was added to freeze-dried coffee powder (a commercial product) to make a 0.01 % solution when dissolved in hot water (concentration at drinking). A sensory evaluation was conducted by 6 specialized panels. Coffee containing thiazolidine compound was stronger in preferable flavor compared with plain coffee. The effect continued even 30 minutes after coffee preparation.

**Practical example 12:** synthesis of 2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carboxylic acid

(Omission)

**Practical example 13:** synthesis of 2-methyl-3-furanthiol cysteine disulfide (MFT-Cys)

(Omission)

**Practical example 14:** synthesis of 2-furylmethanethiol cysteine disulfide (FFT-Cys)  
(Omission)

**Practical example 15:** synthesis of 2-(1-mercaptoethyl)furan cysteine disulfide (MFF-Cys)  
(Omission)

**Practical examples 16-18:** Sensory evaluations on dissolved chicken bouillon cube. A non-volatile thiazolidine compound, prepared by the method described in the practical example 12, was added to a chicken bouillon cube solution (2 cubes (14 g) of commercial chicken bouillon product was dissolved into 600 ml of hot water) to make a 5 ppm solution (concentration at eating). A sensory evaluation was conducted by 5 specialized panels. Chicken bouillon with non-volatile thiazolidine compound was more preferable in flavor and less in the deteriorated chicken fat odor, compared with that of plain chicken bouillon.

**Practical examples 19-20:** Sensory evaluations on dissolved corn cream soup powder.  
(Omission)

**Practical example 21:** A sensory evaluation on instant Miso soup.  
(Omission)

**Practical example 22:** synthesis of 2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carboxylic acid  
(Omission)

**Practical example 23:** synthesis of 2-methyl-3-furanthiol cysteine disulfide (MFT-Cys)  
(Omission)

**Practical example 24:** synthesis of 2-furylmethanethiol cysteine disulfide (FFT-Cys)  
(Omission)

**Practical example 25:** synthesis of 2-(1-mercaptoethyl)furan cysteine disulfide (MFF-Cys)  
(Omission)

**Practical examples 26-29:** Sensory evaluations on frozen Hamburg steak. A non-volatile thiazolidine compound, prepared by the method described in practical example 22, was added to Hamburg steak (a commercial product; 20 g) to make 20 ppm concentration at eating. A sensory evaluation was conducted by 5 specialized panels. Hamburg steak containing non-volatile thiazolidine compound was more preferable in flavor and less in unpleasant meat odor, compared with that of plain Hamburg steak.

**Practical example 30:** synthesis of 2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carboxylic acid  
(Omission)

**Practical example 31:** A sensory evaluation on retort meat sauce.

A non-volatile thiazolidine compound, prepared by the method described in practical example 30, was added to a meat sauce (raw materials: minced beef, onion, carrot, celery, garlic, tomato paste, tomato, beef bouillon, salt, sugar, water) to make 100 ppm concentration at eating. Then, the prepared meat sauce was packed in a pouch, sealed, and heated at 123 degrees Celsius for 15 minutes (retort treatment). A thiazolidine-free meat sauce product was prepared using the same procedure, and utilized as a control. A sensory evaluation was conducted by 6 specialized panels. A retort meat sauce containing non-volatile thiazolidine compound was more preferable in flavor and less in unpleasant retort odor, compared with that of plain retort meat sauce.

**Practical example 32:** synthesis of 2-(1,2,3,4-tetrahydroxybutyl)thiazolidine-4-carboxylic acid  
(Omission)

**Practical example 33:** A sensory evaluation on retort meat sauce.

A non-volatile thiazolidine compound, prepared by the method described in practical example 32, was added to a 5 % soy protein solution to make 100 ppm concentration. Then, the solution was heated at 100 degrees Celsius for 1 hour. A thiazolidine-free soy protein solution was prepared by using the same procedure, and utilized as a control. A sensory evaluation was conducted by 5 specialized panels. A soy protein solution containing non-volatile thiazolidine compound was more preferable in flavor and less in grassy odor, compared with that of plain soy protein solution.

**Practical examples 34-36:** Sensory evaluations on Hamburg steak containing soy protein.  
(Omission)

### **An estimated mechanism of thiazolidine compounds in enhancing or improving the flavor of foods or drinks**

As shown in formula 1, a non-volatile thiazolidine compound (a) generates 2-aminoethanethiol derivatives (b) by an equilibrium reaction. In formula 1, R1, R2, R3, and R4 mean individual functional groups, such as alkyl group, aryl group, carboxyl group, and proton that are binding to the cyclic structure of a thiazolidine molecule by hydrogen atoms or carbon atoms. The generated aminoethanethiol derivatives (b) cut reductively the sulfide bonds in foods and drinks, due to the reducibility of the thiol group. As a result, it makes free volatile thiol compounds with disulfide bond in foods or drinks. These free volatile thiol compounds strengthen the flavor. Moreover, the generated aminoethanethiol derivatives (b) also generate other flavors by chemical reactions caused by heating, etc. Aminoethanethiol derivatives (b) are generated from thiazolidine compounds (a) continuously, little by little, by an equilibrium reaction, since the derivatives generated are consumed gradually by chemical changes such as a reductive cut of disulfide bonds, etc. Therefore, the effect in enhancing or improving the flavor of foods or drinks is retained for a long period, and the amount of flavor can be regulated by the added amount of non-volatile thiazolidine compounds. Volatile thiol compounds are easily oxidized, and thiol compounds contained in foods or drinks are easily lost during storage. However, thiazolidine compounds described in this patent are more stable than thiol compounds, and this is advantageous when added to foods or drinks.